# BUREAU INTERNATIONAL DES POIDS ET MESURES



# **International Comparison of Iodine Cells**

by

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#### Abstract

Results of an international comparison of iodine absorption cells organized by the BIPM are reported. Ten of the thirteen member laboratories of the Comité Consultatif pour la Définition du Mètre (CCDM) participated.

Two experimental methods were used to estimate the purity of the iodine in the cells: first, the cells were incorporated in BIPM He-Ne lasers and the laser frequencies thus obtained at  $\lambda = 633$  nm were compared by the beat frequency method with those of the BIPM reference lasers and, second, direct measurements of iodine purity by a laser induced fluorescence method were made at  $\lambda = 502$  nm.

Of the thirty nine cells investigated more than half are pure enough to realize a frequency reproducibility to within 10 kHz (2 parts in  $10^{11}$  in relative terms).

A particular contamination has been observed in certain cells : the comparison confirms that observed frequency shifts of the hyperfine components in iodine are strongly linked to impurities in the iodine cells.

## Résumé

Nous présentons les résultats d'une comparaison internationale de cuves d'absorption d'iode organisée par le BIPM et à laquelle dix des treize laboratoires membres du Comité consultatif pour la définition du mètre (CCDM) ont participé.

Deux méthodes différentes ont été utilisées pour estimer la pureté de l'iode dans les cuves : d'une part, par des mesures de battements entre les radiations émises à  $\lambda = 633$  nm de lasers à He-Ne du BIPM dans lesquels les cuves ont été installées et celles des lasers de référence du BIPM et d'autre part, par des mesures directes de la pureté de l'iode en utilisant une méthode de fluorescence induite à l'aide d'un laser à argon à  $\lambda = 502$  nm.

Sur les trente-neuf cuves qui ont été étudiées plus de la moitié d'entre elles ont une qualité suffisante pour assurer une reproductibilité de fréquence meilleure que 10 kHz (2 x  $10^{11}$  en valeur relative).

Nous avons observé sur certaines cuves une contamination inhabituelle. La comparaison a confirmé que les décalages de fréquence observés des composantes hyperfines de l'iode sont essentiellement produits par les impuretés contenues dans les cuves.

# **Table of contents**

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	Pages
1. Introduction	4
2. Experimental technique	5
2.1 Beat frequency measurements	5
2.2 Laser induced fluorescence measurements	6
3. Results	7
4. Discussion	14
Conclusion	15
Acknowledgement	15
References	16
Appendix I	
Appendix II	
Appendix III	
Appendix IV	
Appendix V	
Appendix VI	

### 1. Introduction

The definition of the metre is based on a conventional value for the speed of light [1] and a set of recommended frequencies of molecular transitions. The metre may be realized using any of the five recommended frequencies, all corresponding to hyperfine transitions: four in iodine and one in methane [2]. Stabilized lasers are used to generate these frequencies. The most popular laser for metrological applications is the He-Ne laser stabilized at a wavelength  $\lambda = 633$  nm. This is because of its wide commercial availability, its emission in the visible, and the possibility of mechanical compactness. Its radiation corresponds to the 11-5 R(127) line of the B-X system in  ${}^{127}I_2$ , one of whose hyperfine components i is among the recommended frequencies mentioned above.

The most common way of stabilizing a He-Ne laser in the visible is by means of a glass cell filled with iodine, placed either inside or outside the laser cavity. By modulating the laser frequency through the saturated absorption of the iodine vapour, a signal at three times the modulation frequency is detected to give a third derivative line profile. Using this signal, it is possible to stabilize the laser very precisely onto a hyperfine component which precision then determines the precision of the frequency of the laser radiation.

It has been shown however, that several effects can influence the hyperfine frequency : these include the amplitude of the laser frequency modulation [3], the iodine pressure [3], the laser intracavity power [3], the wavefront geometry [4], the direction of the laser beam propagation [5], gas lens effects [6], contamination of the reference gas [7-12] and even dirty laser optics [13]. Among these effects, it has been observed that frequency shifts of the hyperfine components are strongly correlated with concentrations of foreign gas molecules in the iodine cell and this represents one of the most important factors influencing the measured hyperfine frequency.

The BIPM decided to organize an international comparison of iodine cells, to provide the base for monitoring long-term changes in individual iodine cells, and to check the relation between frequency shift and impurity concentration on a larger scale. All member laboratories of the CCDM were invited to send some of their cells to the BIPM during the period December 1990 - May 1991. Most member laboratories expressed their interest in such a comparison and replies to a questionnaire circulated in 1990 are reproduced in Appendix I.

Ten out of thirteen invited laboratories sent a total of 28 glass cells for measurement, 26 were filled with  ${}^{127}I_2$  and 2 with  ${}^{129}I_2$ . The participating laboratories

were CSIRO (Australia), IMGC (Italy), INM (France), KRISS (former KSRI) (Rep. of Korea), NIM (People's Rep. of China), NIST (Gaithersburg, USA), NPL (UK), NRC (Canada), NRLM (Japan) and PTB (Germany). Eleven cells from the BIPM were also measured during the comparison. Five of this latter group have a known rate of pollution and were used as reference cells.

Individual laboratories were asked to describe the method used to fill their iodine cells, and to give the dates on which this had been done. This information is reported and analyzed in Appendix II.

Although this comparison was time consuming for the BIPM, it was convenient and relatively cheap for the participating laboratories. All cells were sent by post and all were received without damage. Another reason for making this comparison was to study, over a limited period of time, a large sample of cells which differ from each other in geometrical shape and size, in materials, in filling procedures, and in age. During the comparison, we discovered that some laboratories had sent both contaminated cells and good ones: this increased the interest of the comparison.

We chose to use two different techniques for the comparison:

i) The cell was placed in turn in two different He-Ne lasers operating at  $\lambda = 633$  nm in order to create laser systems stabilized to one hyperfine component in iodine. The quality was then measured by the frequency shift relative to one of our reference lasers using the beat frequency technique.

ii) Laser induced fluorescence techniques were used to study the collision-induced quenching in iodine caused by contaminating gases. The concentration of impurities was then determined relative to other cells previously studied.

These techniques are described briefly in the next section. The results are presented in section 3.

## 2. Experimental technique

The reference cells were of different sizes and shapes. All had Brewster windows and cold fingers. Individual cells are identified, and their dimensions given, in Appendix III.

#### 2.1 Beat frequency measurements

The BIPM7 and BIPM11 lasers were chosen for use as test lasers. The BIPM4 laser was used as reference. These lasers were all stabilized using the third harmonic

frequency locking technique [14], and were placed on an optical table protected from vibrations, dust and changes of temperature.

To avoid systematic errors from the laser geometry each cell to be tested was placed within the cavity of the BIPM7 and BIPM11 lasers. The optical parameters of these lasers are similar to those of the BIPM4 laser and have been described elsewhere [15]. Cells were divided into groups of approximatively the same dimensions to avoid time consuming changes in laser cavity geometry. The alignment of individual lasers was adjusted until a maximum output power was obtained. The power was then adjusted to about the level of the reference laser ([139 ± 17]  $\mu$ W) by rotating the body of the iodine cell. The beam from each laser was then superimposed on an avalanche photodiode connected to a frequency counter. The beat frequency between the two lasers, each stabilized on two separate hyperfine transitions, was measured by a computerized system.

Each set of measurements consisted of a matrix of measurements in which the frequency differences between all possible combinations of the d, e, f, and g hyperfine components were measured, except for the same components (e - e, f - f, etc. [16]). The individual components for each cell were also recorded on a chart recorder to check the signal-to-noise ratio and D.C. offsets (see Appendix IV). At least two, and usually several, matrix measurements were performed for each cell on each test laser. For each set of measurements, the alignment of the gain tube and the iodine cell was re-set in order to avoid systematic errors and to obtain independent measurements.

## 2.2 Laser induced fluorescence measurements

It can be shown that induced fluorescence of a contaminated gas sample is more sensitive to pressure changes than one which is pure due to the quenching of fluorescence by collisions. This fact can be used to estimate the relative impurity concentration of a gas sample, through the relationship

$$\frac{I_0}{I_F} = K_0 \frac{1}{p_I} + L_0, \qquad (1)$$

where  $I_F$  is the fluorescence intensity,  $I_0$  is a normalizing parameter,  $p_I$  is the iodine pressure and where  $K_0$  is a coefficient and  $L_0$  is a factor. This is a normalized form of the Stern-Volmer formula [17]. It can be shown that  $K_0$  is a function of the foreign gas pressure,  $p_x$ ; the larger  $p_x$ , the larger  $K_0$ , provided that all other experimental parameters are kept constant [18]. If the iodine cell is filled to the sublimation limit, it is easy to control its gas pressure by cooling a small part of the cell, usually called the cold finger. Laser induced fluorescence at  $\lambda = 502$  nm (Ar<sup>+</sup> laser line) was measured as a function of the cold finger temperature, the temperature being converted into pressure. Parameters  $K_0$  and  $L_0$ were then fitted to experimental data. In this way the pressure of the contaminant gas in each cell may be estimated from the measured value of  $K_0$ . Two sizes of cooling apparatus had to be used due to the different cold finger dimensions of the cells. Typically three or four measurements were performed for each cell. Consecutive measurements were not made on individual cells. For further experimental details, see [12, 18].

# 3. Results

The data obtained represents more than two hundred sets of measurements and one hundred and twenty five fluorescence measurements, so only the means of the measurements and their standard deviations are given here. The complete data for each participating laboratory has been distributed to the laboratory concerned.

To describe the data we denote the frequency shift obtained by the beat frequency measurements by  $\Delta v$ , and its standard deviation s ( $\Delta v$ ). Similarly, we describe the relative impurity concentration obtained by the fluorescence measurements by the coefficient  $K_0$  and its standard deviation by s ( $K_0$ ). The results are listed in Table 1 for each laboratory and cell.

Table 1. Results from measurements of frequency shift and impurity rate of iodine cellsDecember 1990 - May 1991.

Laboratory	Cell	$[\Delta v \pm s (\Delta v)] / kHz$	$[K_0 \pm s \ (K_0)] \ / \ Pa$
CSIRO	1	$+ 1,6 \pm 2,7$	1,70 ± 0,06
IMGC	2	$-16,1 \pm 4,3$	(e)
	30	$-40,1 \pm 1,7$	$4,51 \pm 0,06$
INM	6	$-17,8 \pm 1,4$	(e)
	9	$-5,4\pm2,7$	$2,26 \pm 0,03$
	12	$-20,8 \pm 4,0$	$3,54 \pm 0,11$
INM	DI	$-0,2 \pm 3,8$	$1,21 \pm 0,04$
INM	LAC	$-3,8\pm6,6$	(e)

Laboratory	Cell	$[\Delta v \pm s (\Delta v)] / kHz$	$[K_0 \pm s \ (K_0)] / Pa$
KRISS	4	(a)	(a)
	5	(a)	(a)
	115	$-0,5 \pm 1,0$	$0,94 \pm 0,08$
NIM	II	$-1,6 \pm 1,1$	(e)
	III	$-3,7 \pm 1,5$	(e)
NIST	1	9,9 ± 2,2	(b)
NPL	5C	$-2,9 \pm 1,7$	$1,79 \pm 0,14$
	MOM3e	$-27,0 \pm 6,1$	$3,78 \pm 0,15$
	МОМ2Ъ	$-14,9 \pm 3,6$	1,59 ± 0,39
	5A	- 6,7 ± 5,0	$2,29 \pm 0,11$
NRC	7-12	-286,4 ± 6,7	5,81 ± 0,30
	7-13	$-14,1 \pm 6,9$	$2,99 \pm 0,14$
	9-1	(c)	(c)
	9-2	(c)	(c)
NRLM	1	$2,3 \pm 7,1$	$1,44 \pm 0,02$
	2	$-3,5 \pm 2,0$	$1,31 \pm 0,12$
	3	$2,0 \pm 1,8$	$1,30 \pm 0,29$
РТВ	17/87	$-2,7 \pm 1,2$	$1,26 \pm 0,01$
	16/89	2,6 ± 2,8	$1,05 \pm 0,07$
	7/90	- 5,2 ± 3,3	$1,04 \pm 0,08$
BIPM	1	$-4,6 \pm 0,4$	(d)
	35	$-39,2 \pm 0,6$	$4,70 \pm 0,13$
	64	$-10,4 \pm 4,3$	$2,19 \pm 0,11$
	67	$-6,0 \pm 4,0$	$3,16 \pm 0,19$
	71	$-26,0 \pm 9,0$	$4,07 \pm 0,06$
	88	(d)	$1,53 \pm 0,02$
	95	7,8 ± 5,1	$1,52 \pm 0,08$
	106	$4,9 \pm 0,7$	$1,95 \pm 0,14$
	107	$-3,9 \pm 1,4$	$1,21 \pm 0,03$
	112	- 7,6 ± 3,3	(d)
	JAEGER	-133,8 ± 3,7	$6,30 \pm 0,15$

(a) No iodine was detected.
(b) No cold finger was available.
(c) Glass cell containing <sup>129</sup>I<sub>2</sub>; see the results below.
(d) The iodine cell was not accessible.

(e) Unexpected fluorescence effect; see text.

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We illustrate the distribution in quality by the histograms shown in Fig. 1. Figure 1a shows a histogram of the measured frequency shifts: twenty-two of the thirty-four fall within  $\Delta v = \pm 10$  kHz. Figure 1b shows the histogram of  $K_0$  for the same cells: sixteen of the twenty-seven cells have a  $K_0$  of less than 2 Pa. We consider these cells to be acceptable for use in maintaining a precise frequency standard.

It may be that cells sent for measurement are used to maintain a national frequency standard, and therefore are selected as good. This would explain why a high fraction of the cells showed small values of  $\Delta v$  and  $K_0$ . We suspect also that cells found to have a poor performance were deliberately chosen for the exercise, just because they have shown problems.



Fig. 1a.- Histogram showing the distribution of measured frequency shift  $\Delta v$  in the iodine cells using BIPM7 as the test laser. Nearly 60 % of the cells show a total frequency shift within ± 10 kHz.



Fig. 1b.- Histogram showing the distribution of the measured relative impurity coefficient  $K_0$ . Nearly 60 % of the cells show a  $K_0$  of less than 2 Pa.

In the fluorescence measurements, an unexpected effect was observed in five of the cells; these were NIM-II, NIM-III, IMGC-2, INM-6, and INM-LAC. In these cells the fluorescence did not decrease on cooling the iodine trap. On the contrary it would oscillate when the temperature of the cold finger was held below room temperature and even increase when the temperature applied to the cold finger was stable. During the frequency shift measurements, lasers were allowed to stabilise thermally over several hours.

Among the twelve cells, IMGC-2, INM-LAC, INM-D1, INM-12, NPL-MOM3e, NPL-5A, NPL-MOM2b, NRC-7-13, NRC-7-12, NRLM-1, BIPM-64, and BIPM-71, from which we obtained a large standard deviation in the frequency shift measurements, eight certainly contain gaseous impurities; they present both a large frequency shift and a high  $K_0$  (see table 1). From the large value of these standard deviations we infer that the quantity of condensed foreign gas differs between measurements of the same cell, an effect that can arise if the cell is not filled to saturation. The INM-6 cell showed a large shifts and a small standard deviations. The two cells from NIM which showed

small frequency shifts and small standard deviations have very narrow cold finger tips. Could a thermal effect explain why the fluorescence measurements from these two cells did not turn out well ?

An interesting feature was observed in two of the three cells coming from the PTB namely PTB-16/89 and PTB-7/90. Similar cells were mounted on several lasers used during a recent intercomparison in which the BIPM participated [19]. During the comparison, wider frequency distributions than usual were measured in the components of these laser systems. Our measurements confirm this observation on BIPM lasers equipped with the PTB cells. We therefore believe that these wide distributions come from the iodine cell itself rather than from the laser system. The effect is illustrated in Fig. 2, where the frequency difference of the d, f, and g components from the recommended value is plotted for each measured cell. These differences were estimated by fitting the measured frequency differences using a least-squares method (see Appendix V), and considering the e component as origin.

We have used only the results of the measurements made with the BIPM7 laser but it should be noted that those made with the BIPM11 laser lead to similar results (*see* Appendix VI). The recommended values are listed in the document attached to the new definition of the metre [2]. The d component always shows a positive difference, while the f, and g components are mostly negative. The mean and its standard deviation are marked for each line in the figure. As the standard deviation given in the document defining the metre is 5 kHz, the mean values of these differences fall within one standard deviation. It is worth noting that for all the cells the frequency shift of the d and g components is partly due to the neighbouring component. A particularly large deviation was found for the two PTB cells mentioned above but a large deviation was also found for one of the NRC cells, cell NRC-7-12.

To analyse the results from these three cells, we may link the irregular distribution of the d, e, f, and g components to a possible weak contamination of <sup>127</sup>I<sub>2</sub> by <sup>129</sup>I<sub>2</sub>. This is suggested by the frequency coincidence of components d, e, f, and g (or  $a_{18}$  to  $a_{15}$ ) of 11-5 R(127) of <sup>127</sup>I<sub>2</sub> and the components d,  $g_1$ , h (or  $m_{17}$ ,  $m_{14}$ , and  $m_{12}$ ) of 6-3 P(33) of <sup>127</sup>I<sup>129</sup>I (see [2] Tables 8 and 14). Both the <sup>129</sup>I<sub>2</sub> and <sup>127</sup>I<sub>2</sub> isotopes contribute to the fluorescence signal, both are influenced by the controlled iodine pressure  $p_1$  and they should have about the same self collision cross section. Even if the lifetime of <sup>129</sup>I<sub>2</sub> differs from that of <sup>127</sup>I<sub>2</sub> for the exciting wavelength being used, its influence will be difficult to distinguish from <sup>127</sup>I<sub>2</sub> itself in absence of other impurities, using our measurement methods. It is not surprising therefore that the measured  $K_0$  is small for the PTB cells.



Fig. 2.- Diagram showing the frequency difference  $\Delta v$  of the d, f, and g hyperfine components from the recommended value [2] using the hyperfine component e as origin for each measured cell. The d component is represented by o, the f component by  $\bullet$ and the g component by  $\Delta$ . The individual calculated standard deviation for each component obtained from the fitting is marked as an error bar. The overall mean value and the standard deviation for  $\Delta v$  for each component is depicted by full and dashed lines respectively, shown on each side of the figure. These measurements are obtained using the BIPM7 as test laser.

Since the filling system at the NRC is known to have been used for both iodine isotopes, we suggest that the observed frequency shift in the NRC-7-12 cell has this as its origin.

Two  $^{129}I_2$  cells were sent by the NRC. We did not obtain a laser oscillation when using the NRC-9-1 cell, but using the NRC-9-2 cell with the BIPM7 laser and comparing its with the BIPM4 laser, the results were as follows.

For the each cold finger temperature stabilized at :

i) 12 °C;  $f(k, 8-4 P(54), {}^{129}I_{2}) - f(i, 11-5 R(127), {}^{127}I_{2}) = 95,81 \text{ MHz}$ 

ii) 15 °C;  $f(k, 8-4 P(54), {}^{129}I_9) - f(i, 11-5 R(127), {}^{127}I_9) = 95,84 MHz.$ 

The reference value given in [2] is :  $[95,90 \pm 0,04]$  MHz.

The frequency reproducibility of a laser using an iodine cell filled with  ${}^{129}I_2$  is usually worse than that obtained with a laser using an iodine cell filled with  ${}^{127}I_2$ . This is caused by the difficulty in obtaining pure  ${}^{129}I_2$ : there are always variable and unknown fractions of  ${}^{127}I_2$ . Other frequency perturbations have already been observed on the k component [20]. Four components of  ${}^{129}I_2$ , 12-6 P(69), and twenty-four components of  ${}^{127}I^{129}I$ , 6-3 P(33), have also been also measured [2].

Finally, we show the measurements of frequency shift and relative impurity content, as first suggested by Spieweck [9], in Fig. 3. The tendency of this curve corresponds to earlier results [9, 12], that is, small frequency shifts correlate with small impurity fractions. For higher fractions the estimate is uncertain. We have observed a shift of the curve that may be due to a frequency reproducibility of the BIPM lasers which is given to  $\pm$  5 kHz including the installation of a new gain tube for the BIPM2 laser. Positive values of  $\Delta f$  may also indicate a weak contamination of the BIPM iodine reference cells.



Fig. 3.- Measured values of the hyperfine component frequency shift  $\Delta v$  and the relative impurities rate  $K_0$  for twenty-four cells. The results correspond well with earlier observations [9, 12].

# 4. Discussion

Before and after the comparison we received reports from some laboratories on the behaviour of their cells. We know that all the cells were returned without damage.

The CSIRO cell was remeasured with two others after its return to Australia. The results agree to within the experimental error ( $\pm$  5 kHz). They also agree well with those obtained at the BIPM.

The frequency shifts obtained at the IMGC for cells 2 and 30 before the comparison were respectively :  $[-0.8 \pm 5]$  kHz and  $[-30.7 \pm 5]$  kHz. These values differ from those obtained at the BIPM by respectively - 15 kHz and - 10 kHz.

The INM-6 and INM-12 cells had already been checked at the BIPM in 1981 [7], the results were respectively - 6,1 kHz and - 17,5 kHz. The new values are - 17,8 kHz and - 20,8 kHz.

For the NPL, the frequency differences of cells MOM3e and 5A were : i) at the NPL, in 1984; MOM3e - 5A = - 24,6 kHz; ii) at the BIPM, in 1991; MOM3e - 5A = - 20,3 kHz.

For the MOM2b cell, the frequency difference at the NPL was + 5,7 kHz when compared with a good cell, in 1980; and - 1,6 kHz at the BIPM in 1981 [7]. This cell seems have deteriorated slightly, the actual value is - 14 kHz.

At the NRLM, the three cells were found to be within the measurement uncertainties ( $\pm$  5 kHz) as at the BIPM.

It is also worth noting that the BIPM-1 cell, filled in September 1972 and still used on the BIPM2 laser, showed a frequency shift of only  $[-4,6 \pm 0,4]$  kHz.

The PTB noted before the comparison that there is some hint that the 7/90 cell may be slightly contaminated. This has not been confirmed as clearly by the frequency shift measurements as by the induced fluorescence measurements; a frequency shift of - 7,8 kHz, however, has been observed between the 7/90 and 16/89 cells. Nevertheless, on the 7/90 the largest distribution of frequency has been observed between the components d, e, f, and g and specially between the components d and f, around 20 kHz (see Fig. 2).

No laboratory other than the BIPM has to our knowledge performed laser induced fluorescence measurements on these cells.

## Conclusion

We have studied a large number of iodine cells many of which are used to maintain present national wavelength and optical frequency standards. Almost all the cells have been measured in two independent ways within a limited time frame against the same references. It has been encouraging to find that for both methods, the majority of cells lie within a narrow range corresponding to  $\pm 10$  kHz (2 parts in  $10^{11}$ ).

In a systematic way we have also confirmed that cell contamination is an important contributor to frequency shifts in recommended radiations based upon iodine stabilized lasers.

Concerning the shape of the cells, we think that cold fingers which are too short or too narrow can lead to a poor definition of the iodine temperature and consequently to poor frequency reproducibility.

The use of natural  $^{127}\mathrm{I}_2$  is preferable to that of  $^{129}\mathrm{I}_2$  even though the latter has a stronger absorption due probably to the difficulty of obtaining cells filled with pure  $^{129}\mathrm{I}_2$ .

The cells measured in this study used the BIPM standards in a convenient way and provide useful data for future comparisons. Such comparisons are helpful for all the laboratories concerned because they provide a check on the stability with respect to time which may be confirmed periodically, perhaps every five years. We hope that this comparison will contribute to the improvement and maintenance of the present wavelength and frequency standards.

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# Appendix I

The following questionnaire was addressed the 3 April 1990 to all the member laboratories of CCDM.

These laboratories were :

CSIRO	Australia
IMGC	Italy
INM	France
KRISS	Korea (Rep. of)
NIM	China (People's Rep. of)
NIST	Gaithersburgh, U.S.A.
NIST - JILA	Boulder, U.S.A.
NPL	United Kingdom
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BIPM comparison of iodine cells

### Preliminary questionnaire, April 1990

Name<sup>+</sup> :

Organization :

Adress :

Telephone Telefax Telex

+ Unless advised otherwise, all future correspondence concerning the comparison will be sent to the person named here.

1. Are you interested in participating in the BIPM comparison of iodine cells ?

# YES NO

2. If so, is the proposed period of the comparison, the end of 1990, convenient.

YES NO

If not when would you like it to take place :

3. How many cells would you like to submit :

$$127$$
I<sub>2</sub> cells  
 $129$ I<sub>2</sub> cells

4. Dimensions of cells

Length :

Diameter :

Please enclose an approximate sketch of your cells.

5. Do you have any question or comments ?

.

# Please return this form by 1st July 1990 to

Monsieur le Directeur Bureau International des Poids et Mesures Pavillon de Breteuil F-92312 SEVRES Cedex (France)

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## Appendix II

Iodine cells filling methods of some laboratories:

- Perturbations de l'iode moléculaire en phase vapeur par la présence de gaz étrangers conséquence pour la stabilisation du laser He-Ne, G. Flory, M. Broyer, J. Vigue et J.C. Lehmann, Ecole normale supérieure, Paris (France).
- Notes on iodine cell construction and filling procedure, N. Brown, CSIRO (Australia).
- 3 Arguments presented by NIST concerning the status of iodine stabilized lasers, H.P. Layer, NIST (USA).
- 4) The preparation and Analysis of iodine cells, P. Gill and R.C. Thompson, NPL (U.K.).
- 5) NRC Iodine Cells, G.R. Hanes, NRC (Canada).
- How to refine and fill iodine 127 into the cell at NRLM, T. Sakurai, S. Iwasaki, T. Kurosawer and K. Tanaka, NRLM (Japan).

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- 7) Filling procedure at PTB, J. Helmcke and H. Darnedde, PTB (Germany).
- 8) Iodine cells preparation at BIPM, J.-M. Chartier and F. Perez, BIPM.

Classification Physics Abstracts 5.446 - 5.448 - 0.460

# PERTURBATION DE L'IODE MOLÉCULAIRE EN PHASE VAPEUR PAR LA PRÉSENCE DE GAZ ÉTRANGERS CONSÉQUENCE POUR LA STABILISATION DU LASER He-Ne

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(Reçu le 28 décembre 1976, accepté le 8 février 1977)

Résumé. — Une méthode très sensible de mise en évidence des impuretés gazeuses dans les cellules d'iode moléculaire est présentée et appliquée. Les résultats prouvent la grande importance de ces impuretés. Nous montrons que la présence de ces gaz peut limiter la reproductibilité de la stabilisation sur l'iode du laser He-Ne. Une technique pour obtenir des cellules très propres est décrite et la qualité des cellules obtenues ainsi est analysée.

Abstract. — A very sensitive method to test the presence of gaseous impurities in molecular iodine cells is presented and applied. The results prove the great importance of these impurities. It is shown that the presence of these gases can limit the reproducibility of the He-Ne laser stabilized on iodine. A technique to fill very clean cells is described and the quality of such cells is discussed.

1. Introduction. — Depuis plusieurs années, de nombreuses équipes [1] ont développé et amélioré le procédé de stabilisation en fréquence de la raie 6 328 Å d'un laser He-Ne monomode sur l'un des pics d'absorption saturée de la vapeur d'iode moléculaire. Un étalon secondaire de longueur en est déjà résulté dont la reproductibilité avoisine  $10^{-11}$ .

Nous voulons attirer l'attention dans cette publication sur des limitations possibles de cet étalon dues à des effets de collisions sur des impuretés gazeuses, très fréquemment présentes dans les cellules scellées remplies d'iode.

2. Mise en évidence de gaz étrangers dans les cellules d'iode. — La mesure de la durée de vie  $\tau$  d'un niveau moléculaire excité constitue un test de la présence de gaz étrangers. En effet, l'inverse y de cette durée de vie peut s'écrire :

$$\gamma = \frac{1}{\tau} = \frac{1}{\tau_0} + \frac{V_{rI_2I_2^*}}{kT} \sigma_{I_2I_2^*}^{\mathsf{E}} p_{I_2}(T_f) + \sum_{A} \frac{V_{rAI_2^*}}{kT} \sigma_{AI_2^*}^{\mathsf{E}} p_{A}(T_f)$$

 $\tau_0$  désigne la durée de vie en l'absence totale de collisions ;  $I_2^*$  désigne l'iode excité et  $v_{rXY}$  la vitesse relative moyenne des espèces X et Y;

 $\sigma^{\rm E}$  est la section efficace de destruction de la population du niveau excité de  $I_2$  due aux collisions  $I_2 I_2^*$  ou  $AI_2^*$ .

Enfin,  $T_f$  est la température du point froid de la cellule et  $p_A(T_f)$  la pression de l'espèce atomique ou

moléculaire A présente dans la cellule; on a forcément  $p_A(T_f) \leq p_A^S(T_f)$  où  $p_A^S(T_f)$  désigne la pression de vapeur saturante de l'espèce A à la température  $T_f$ . L'iode est supposée toujours en vapeur saturante. T est la température de la cellule, constante et toujours supérieure à  $T_f$ ; k est la constante de Boltzmann.

Le rapport signal sur bruit de toute mesure de  $\gamma$  tend vers zéro lorsque  $p_{I_2}$  tend vers zéro; l'étude de  $\gamma$  ne peut se faire que pour  $p_{I_2} > p_0$  soit  $T_f > T_0$ . La zone  $T_f < T_0$  est inaccessible pratiquement (En général, pour nos mesures, l'ordre de grandeur de  $p_0$  est de 2,5 mtorr ce qui correspond à  $T_0 = -22$  °C). La formule utilisée pour relier  $p_{I_2}$  à  $T_f$  est celle de Baxter et Grose [2]

$$\left(\log p_{l_2}(\text{torr}) = 9,7522 - \frac{2863,54}{273 + t - 19}; t \text{ en }^{\circ}\text{C}\right).$$

Si la cellule ne contient que de l'iode,  $\gamma$  est une fonction linéaire de  $p_{I_2}$  et l'extrapolation linéaire de  $\gamma$  en fonction de  $p_{I_2}$  donne  $\gamma_0 = 1/\tau_0$ . C'est le cas idéal représenté par la courbe 1 sur la figure 1.

Si la cellule contient une seule impureté A, en quantité faible, il existera une température du point froid  $T_A$  en dessus de laquelle l'impureté A sera en vapeur sèche de pression fixe  $p_A = p_A^S(T_A)$ ; pour  $T_f$  inférieur à  $T_A$  nous admettrons que  $p_A(T_f) = p_A^S(T_f)$ ; ceci est une bonne approximation s'il ne se produit pas de réaction chimique entre l'iode solide et la phase solide



FIG. 1. — La dépendance théorique de  $\gamma$  en fonction de la pression d'iode est représentée dans 3 cas. (L'échelle des abscisses est linéaire pour  $P_{I_2}$  et non linéaire en  $T_{I_2}$ ) Courbe 1 : cellule sans gaz étrangers. Courbes 2 et 3 : cellule avec gaz étrangers en vapeur sèche pour  $T_I > T_{A_2}$  et  $T_{A_3}$  respectivement.

[The theoretical dependence of  $\gamma$  as a function of the iodine pressure is plotted in 3 cases. (The horizontal scale is linear in  $P_{I_2}$  and non linear in  $T_f$ ): Curve 1: cell free from foreign gases; Curves 2 and 3: cell with foreign gases in unsaturated vapour for  $T_f > T_{A_2}$  and  $T_{A_3}$  respectively.]

ou liquide de A.  $\gamma$  en fonction de  $p_{I_2}$  est alors représenté par une droite pour  $T > T_A$ , alors qu'au-dessous de  $T_A$ , la forme de  $\gamma$  n'est pas simple, sauf si  $p_A(T_f)$  et  $p_{I_2}(T_f)$  sont proportionnels, auquel cas  $\gamma$  y est encore représenté par une droite. Les courbes 2 et 3 de la figure 1 représentent ce cas avec soit  $T_{A_2} > T_0$  soit  $T_{A_3} < T_0$ .

Les courbes 1 et 2 conduisent à la même valeur extrapolée de y mais avec des pentes différentes dans la zone  $T_f < T_{A_2}$ . La courbe 3 s'extrapole à

$$\gamma_3 = \gamma_0 + \frac{V_{rAI_2}}{kT} p_A \sigma_{AI_2}^{\mathrm{E}}$$

car la zone  $T < T_0$  n'est pas explorée. On voit donc que la comparaison des valeurs extrapolées de  $\gamma$ obtenues pour des cellules différentes sera sensible à la présence d'impuretés telles que  $T_A < T_0$ . Si au contraire  $T_A > T_0$ , ce ne sera que la pente  $\delta \gamma / \delta p_{I_2}$  qui sera sensible à la présence de l'impureté A.

Nous disposons donc d'une méthode de mise en évidence des impuretés. Cette méthode sera d'autant plus sensible que le terme  $\gamma_0$  sera plus petit et que les sections efficaces seront grandes. L'iode est un cas très favorable dans la mesure où lorsqu'on s'approche de la limite de dissociation de l'état  $B^3\Pi_{ou}^+$  on trouve des niveaux d'énergie de durée de vie très longue [3]; simultanément ces niveaux sont un peu plus sensibles aux collisions.

Le tableau I compare les durées de vie et les sections efficaces  $I_2$ - $I_2^*$  pour les niveaux  $B^3 \prod_{ou}^+ v' = 11$ J' = 128 (niveau supérieur de la transition servant à l'asservissement du laser He-Ne 6 328 Å) et du niveau v' = 62 J' = 27 excité par la raie 5017 Å du laser Ar<sup>+</sup>. Niveaux  $B^3 \Pi_{ou}^4$ :

v' = 11 J' = 128 [3] v' = 62 J' = 27 [4, 5]

Distance à la limite de dissociation

	3 041 cm	1 - 1	98 cr	n - 1
τ <sub>ο</sub> (μs)	0.410 ± 0	.015	14 -	+ 3
$\sigma_{I,I_2}^{\rm E}$ (Å <sup>2</sup> )	204 <u>+</u>	15	286	<u>+</u> 40

3. Méthodes de mesure des durées de vie. Résultats. — Les deux méthodes que nous avons utilisées sont l'effet Hanle c'est-à-dire la dépolarisation magnétique de la fluorescence [4] et l'observation de la décroissance de la fluorescence suivant une excitation en impulsion [5]. Les résultats sont analogues. Nous pensons cependant que dans le cas du niveau v' = 62 J' = 27, l'effet Hanle peut s'avérer plus pratique car il ne nécessite pas d'électronique rapide mais seulement un champ magnétique assez faible balayable de 0 à 200 G environ.

L'observation de l'effet Hanle donne des courbes de Lorentz d'absorption ou de dispersion en fonction du champ magnétique B, d'équations

$$\frac{1}{1 + (B/B_0)^2}$$
 ou  $\frac{(B/B_0)}{1 + (B/B_0)^2}$ 

La valeur de  $B_0$  est reliée à y par

 $2 g \mu_n B_0 = h \gamma$ 

soit d'après nos mesures du facteur de Landé g [4, 6]

$$B_0(G) = (5,7 \pm 0,2) \, 10^{-5} \, \gamma \, (s^{-1})$$

équation valable seulement pour le niveau v' = 62J' = 27.

La figure 2 montre l'inverse  $\gamma$  de la durée de vie de ce niveau en fonction de la pression d'iode pour deux cellules différentes remplies dans des conditions analogues avec de l'iode  ${}^{127}I_2$ , de haute pureté, après un étuvage de la cellule à 350 °C pendant 24 heures sous



FIG. 2. — Dépendance expérimentale de  $\gamma$  ( $\nu' = 62$ , J' = 27) pour deux cellules remplies dans des conditions différentes. [Experimental dependence of  $\gamma$  ( $\nu' = 62$ , J' = 27) for two cells filled in different conditions.]

un vide meilleur  $10^{-6}$  t. L'iode est introduit par distillation sous vide. Le piégeage a été effectué avec de l'azote liquide (77 K) pour la cellule 1, avec un mélange alcool-carboglace (195 K) pour la cellule 2.

On voit que les pentes des deux droites sont les mêmes mais que les extrapolations donnent des résultats différents. C'est un cas typique où des impuretés sont présentes dans au moins une des deux cellules, ces impuretés ne se condensant pas au-dessus de T = -22 °C. La différence des valeurs extrapolées de  $\gamma$  atteint 10<sup>6</sup> s<sup>-1</sup>.

Ces résultats proviennent de cellules récemment remplies. On constate que les résultats se dégradent avec le temps, c'est-à-dire que  $\gamma$ , extrapolé à pression d'iode nulle, croît.

4. Conséquences de ces résultats pour un étalon de longueur. — 4.1 LARGEUR ET DÉPLACEMENT D'UNE RAIE OPTIQUE DUS AUX COLLISIONS. — On sait que les collisions élargissent et déplacent une transition atomique. Aux faibles pressions (~ 1 torr) ces effets sont très inférieurs à la largeur Döppler, mais tout à fait observables en absorption saturée. Dans le cas de collisions iode-iode, pour la transition B<sup>3</sup>  $\Pi_{ou}^+ \leftarrow X^1 \Sigma_g^+$ 11 – 5 R (127) on trouve que [7, 8]

$$\frac{\delta v}{\delta p_{I_2}} = -1,12 \text{ MHz/torr}$$

$$v = 474 \times 10^6 \text{ MHz}$$

$$\frac{\delta \Delta F}{\delta p_{I_2}} = 8,7 \text{ MHz/torr}$$

v étant la fréquence et  $\Delta F$  la largeur de la transition.

Il n'y a pas d'autres mesures de ces quantités pour l'iode. Mais de nombreuses études de déplacementélargissement ont été faites sur les transitions électroniques atomiques. Il n'existe pas de relation générale entre  $\delta\Delta F/\delta p$  et  $\delta v/\delta p$ ; ni avec  $\delta y/\delta p$  (où y est l'inverse de la durée de vie de l'état excité de la transition).

4.2 EFFET SUR L'ÉTALON DE LONGUEUR D'UNE IMPURETÉ DANS LA CELLULE. — Pour estimer les effets d'une impureté, nous allons admettre que

$$\left(\frac{\delta v}{\delta p_{A}}\right) \left/ \left(\frac{\delta v}{\delta p_{I_{2}}}\right) \simeq \frac{\sigma_{AI_{2}}^{\mathsf{E}} v_{rAI_{2}}}{\sigma_{I_{2}I_{2}}^{\mathsf{E}} v_{rI_{2}I_{2}}}$$

Cette hypothèse revient à admettre que l'impureté Aest équivalente à une certaine pression d'iode  $p_{eq}$ , la même pour la destruction de la population de l'état excité que pour le déplacement de la raie optique. Cette hypothèse nous semble raisonnable pour obtenir un ordre de grandeur. La valeur de  $p_{eq}$  se déduit aisément de la lecture de la figure 2. On trouve  $p_{eq} \simeq 5 \times 10^{-2}$ torr et on en déduit alors le déplacement dû à l'impureté présente dans la cellule 1 (Fig. 2) :

$$\delta v = \left(\frac{\delta v}{\delta p_A}\right) p_A \simeq \left(\frac{\delta v}{\delta p_{I_2}}\right) p_{eq}$$
$$\delta v \simeq 55 \text{ kHz}, \qquad \frac{\delta v}{v} = 1.2 \times 10^{-10}.$$

Ce résultat est un ordre de grandeur du déplacement à craindre pour la raie. Une telle valeur constituerait une limitation essentielle de l'étalon He Ne-iode. Evidemment il est toujours possible que  $\delta v / \delta p_A$  soit très petit. Une étude des déplacements de la raie avec la pression de corps très communs (H<sub>2</sub>O, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>) permettrait d'éclaireir ce point. Une façon probablement plus efficace d'aborder le problème consiste à réaliser des cellules très pures.

5. Méthode de fabrication de cellules très pures. Vieillissement de ces cellules. — Nous avons été amenés à fabriquer des cellules pratiquement exemptes d'impuretés gazeuses afin de pouvoir étudier les niveaux de longue durée de vie du type B<sup>3</sup>  $\Pi_{ou}^+ v' = 62 J' = 27$ .

Nous avons réussi à obtenir de telles cellules par une méthode que nous exposons ci-dessous. Cette méthode, basée sur quelques idées simples, n'est probablement pas la seule. Nous pourrons cependant en affirmer la qualité grâce aux tests très sensibles que sont les mesures de durée de vie du niveau v' = 62, J' = 27.

5.1 RÉALISATION DES CELLULES. — Il faut résoudre deux problèmes :

- 1) bonne qualité initiale des cellules ;
- 2) longue conservation de cette qualité.

Le vieillissement rapide des cellules remplies par la méthode évoquée plus haut est probablement dû à une réaction chimique de l'iode avec la cellule ellemême ou avec les impuretés absorbées dans les parois.

La cellule doit donc tout d'abord être étuvée sous vide ( $p < 10^{-6}$  torr) à 350 °C pendant 24 h. On la remplit alors d'iode par distillation sous vide et la cellule scellée est à nouveau étuvée à 150 °C; la pression d'iode qui y règne alors est d'environ 400 torr, pression de vapeur saturante de l'iode à cette température. Le but de cette opération est de laver les parois, provoquant ainsi par avance les réactions qui pourraient avoir lieu. La cellule est alors remise en relation avec le banc de pompage sans rentrée d'air (par le bris d'une queue de cochon), vidée et réétuvée à 350 °C pendant 24 heures. Cette première partie du traitement permet d'assurer une longue conservation à la cellule. Les valeurs de température sont adaptées aux cellules en pyrex. Elles devraient être modifiées pour des cellules en silice fondue.

Afin d'assurer la propreté initiale, l'iode utilisée pour le remplissage définitif est de haute pureté (par exemple Merck Suprapur) ; il subit d'abord une série de distillations aller et retour entre deux pièges que l'on refroidit alternativement à -60 °C environ. Ceci permet d'éliminer la vapeur d'eau qui est probablement le polluant le plus abondant et le plus volatif de l'iode (les gaz N<sub>2</sub>, O<sub>2</sub>, Ar, CO<sub>2</sub> exceptés) ; en effet  $p_{I_2}$ (-60 °C)  $\simeq 1.4 \times 10^{-5}$  torr tandis que  $p_{H_2O}$ (-60 °C)  $= 8 \times 10^{-3}$  torr. On maintient pendant ce temps un vide meilleur que  $10^{-6}$  torr à la sortie de la pompe. La distillation finale se fait avec un piège refroidi à -40 °C, en veillant tout particulièrement à n'introduire qu'une faible quantité d'iode dans la cellule car les impuretés présentes seront proportionnelles à cette quantité.

5.2 QUALITÉ DE CES CELLULES. — La valeur de  $\gamma$  (v' = 62, J' = 27) extrapolée à  $p_{I_2}$  nulle est égale à  $\gamma_0 = (7 \pm 1) \ 10^4 \ s^{-1}$  reproductible d'une cellule à l'autre. En trois mois, aucun vieillissement n'est décelable à cette précision de mesure.

Sur une période de deux ans de vieillissement  $\gamma_0$  double à peu près. Cet élargissement par gaz étrangers inférieur à 10<sup>5</sup> s<sup>-1</sup> correspond donc à une pression de gaz étrangers plus de 10 fois plus petite que celle de la cellule 1 (Fig. 2) neuve.

La plupart de nos expériences ont utilisé des cellules en pyrex. Les rares essais faits sur des cellules en silice fondue ont semblé prouver qu'elles vieillissaient plus vite que les cellules en pyrex ; cependant notre expérience est trop limitée pour être totalement concluante

designation and the

Il nous semble important qu'une cellule à iode soit testée avec soin. Pour cela si l'on dispose d'un laser à Argon ionisé, l'étude de l'effet Hanle en excitation à 5 017 Å est une méthode très simple. Il faut seulement veiller à ne pas saturer la transition d'absorption ce qui élargirait l'effet Hanle. Une densité de puissance de l'ordre de  $10^{-2}$  W/cm<sup>2</sup>, dans le cas d'un laser multimode est parfaitement adaptée.

6. Conclusion. — Nous pensons avoir apporté dans cette note quelques éléments simples mais importants sur l'influence des phénomènes de collision régnant dans les cellules à iode. La méthode proposée pour obtenir des cellules pures, ainsi que le test suggéré, pourraient se révéler utiles au cas où la stabilisation sur l'iode du laser He-Ne se développerait de façon systématique.

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Notes on iodine cell construction and filling procedure

aldo della

e.m.n.

P 2 2 - 1

The cell is made of pyrex with the Brewster windows welded on using a glass-fritt tape.

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The technique used to fill it follows Flory, Broyer, Vigue and Lehmann ("Perturbation de l'iode moleculaire..." Revue De Physique Appliquee Tome 12, Mai 1977, page 901).

The cell was cleaned in a chromic—sulphuric acid mixture, then washed in de—ionized water and pure alcohol. It was then evacuated and heated to 350°C for 48 hours. Iodine was distilled in and the cell reheated to 150°C to allow any reactions between the iodine and contaminants in the cell to occur. The cell was then pumped out again and heated to 350°C for a further 48 hours before filling. The iodine underwent a series of distillations under vacuum to remove water vapour before a small amount was distilled into the cell.



May 11, 1990

MEMORANDUM FOR Barry N. Taylor Atomic, Molecular, and Optical Physics

FROM: Howard P. Laver Division 460 hoursed Larger

SUBJECT: BIPM Iodine Cell Comparison (Response to Terry Quinn, April 26, 1990)

<u>SUMMARY</u>: The proposed program, to compare existing iodine cells, will be less useful than a program whose purpose is to establish a standard procedure for both cell preparation and testing. The testing program alone will not directly solve the problem of low quality iodine cells.

**<u>BACKGROUND</u>**: Of the many length standard intercomparisons which have been carried out in the past few decades, one ambitious effort stands out. In 1985, Dr. Robert Hurst of the Physical Electronics Laboratory, New Zealand, carried an iodine stabilized HeNe laser around the world and into some ten national The intercomparisons he made indicated that the laboratories. frequencies of all of the lasers tested agreed to better than ±40 Khz  $(\pm 0.9 \text{ parts in } 10^{10})$ . This result was remarkable because of the differences in the operating conditions of the individual lasers and the great diversity of the laser design, construction, and electronic control systems used (PEL Report No. 930). It should be observed that this agreement is well within the uncertainty specified by the BIPM in its document concerning the practical realization of the meter and is a testimony to the strength of the HeNe internal cell stabilization technology.

The results of this series of measurements, however, did not raise much interest in the international metrology community nor stimulate a reappraisal of the present iodine stabilized laser standard either by refining the stated uncertainty or modifying the description of the laser design and operating conditions. Perhaps the reason these results did not stimulate active interest in the national laboratories or the BIPM is that there were no economic or technical forces driving these laboratories to develop a more accurate <u>practical</u> length standard in the visible spectrum sufficient to warrant the investment of limited resources. The value of achieving a much higher <u>laboratory</u> standard using other technology, such as stored ions or atoms, is well recognized and is being actively pursued in several institutions. The extent to which the present HeNe laser length standard satisfies the predictable demand for a practical length standard should be accessed before committing to additional activities.

**PRESENT SITUATION:** The iodine stabilized laser length standard is a mature technology and is unlikely to undergo dramatic additional development. The accuracy that can be achieved is limited by the nature of the physics upon which it is based. It is, however, in very good shape as more than a decade of practical experience has shown. Construction techniques are well understood and widely distributed. Instruments have been built and are being used in both highly and moderately industrialized countries. In its present form, the iodine stabilized laser length standard has sufficient accuracy for all industrial needs including the standardization of gage block based length systems and the calibration of lower stability laser interferometer measuring systems. It also has sufficient accuracy for many scientific applications in atomic and molecular spectroscopy and fundamental constant and base unit measurements where dimensional information is required. Some examples of these are the measurement of the local gravitational constant, the Rydberg constant, the gyromagnetic ratio of the proton, and the calculable capacitor, which is used to define several electrical units.

Most of the physical and instrumental factors which limit the accuracy of the iodine stabilized laser are well understood. Among these are pressure broadening due to impurities in the iodine cell, frequency shifts due to the f.m. modulation index, nonlinearities in the piezoelectric elements, the level of circulating power, and the effect of optical mode shape. However, only a few of these parameters are stipulated in the document concerning the treaty of the meter. Some incremental improvement in the reproducibility of the HeNe laser length standard would be gained if more of its characteristics were standardized.

**PROPOSED PROGRAM:** Although we are in a position to complete the development of the standard for the iodine stabilized laser, it is not clear that is a profitable way to spend a significant amount of time. The accuracies achieved on a worldwide basis with diverse instruments are impressive and are near the attainable limit for reproducibility for that system. All of the needs of the industrial community and many of the needs of the scientific community have been and will continue to be fulfilled for the foreseeable future. Scientific measurements which are not satisfied by the present standard will not be met by small improvements in the iodine stabilized laser but require different technology.

Experience at the BIPM indicates that some lasers, which are otherwise well constructed, fail to perform accurately because of

11221

improperly processed iodine cells. The proposed program to test existing iodine cells will increase information about the extent of the problem, but will not directly create a solution to the problem of defective cell preparation. NIST should propose that the scope of the exercise be expanded and its goal changed to include the development of a procedure for fabrication, processing, and filling iodine cells which will assure their high quality. Such a standard will be useful to any laboratory which makes or uses iodine cells for length of wavelength standards. The present proposal from the BIPM to test cells would be a part of this program.

# The Preparation and Analysis of Iodine Cells

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#### Abstract

The procedure used at NPL for the routine filling of rodine cells is described, along with standard methods employed for the verification of the cells. Results show that a small proportion of the cells filled have significant contamination present. Detailed spectral analysis of these cells identifies the contaminants as primarily  $N_2$  and  $CO_3$ . It is also shown that contaminated cells can be temporarily improved by an extended period of radio-frequency discharge.

#### 1. Introduction

lodine-stabilized lasers have been developed over the past 15 years as sources of a number of highly stable reference frequencies in the visible  $\{1-3\}$ . harly claims for such systems suggested reproducibilities of order 10<sup>-11</sup>. Over the last five years, however, it has been found that careful characterization of the laser and iodine parameters (such as iodine pressure, laser power and beam geometry) is necessary to reach this figure, and more generally a reproducibility level of 10<sup>-10</sup> is attained. More fundamental than the control of these parameters is the basic requirement of adequate purity of the iodine within the sealed absorption cell. A significant background pressure of foreign gas impurities within the sealed cell results in a frequency shift of the iodine saturated-absorption features used for stabilization. This shift is believed to be responsible for certain differences, at the 10<sup>-10</sup> level, noted between iodine- ' stabilized lasers during some international intercomparisons [4]. Thus, both cell preparation and quality control, together with careful control of laser parameters, are of utmost importance in the establishment of the reference standard.

The present article describes the routine preparation, production and verification of iodine cells used in NPL stabilized systems, and the subsequent spectral analysis of these cells. This analysis comprises a spectroscopic assignment of the emission from a mild rf discharge within both pure and contaminated cells. The results show that the major impurities observed to be present in contaminated cells are nitrogen and carbon monoxide.

#### 2. Preparation of Iodine Cells

In recent years, empty absorption cells for use in the various iodine-stabilized lasers at NPL have been filled with iodine-127, in batches of about 10, every year or so. On each occasion the empty cells are glass-blown on to a new pyrex manifold connected to a dedicated pumping system (Fig. 1). The cells are manufactured commercially to a standard design comprising a nominal 13 mm diameter silica tube with 2 mm thick Spectrosil B Brewster windows fused on at each end. The cell lengths are in the range 50-500 mm depending on the application, though 100 mm is normal. Each cell has a 6 mm diameter pyrex side-arm for filling and, in subsequent use, for cooling the iodine solid. Some cells have an extra side-arm, reserved for this cooling.

The source of iodine-127 (sole stable isotope) was a batch-tested, scaled ampoule of triply-distilled iodine [5]. Initially, this ampoule was broken open in a glove box under dry nitrogen and a substantial amount of iodine solid transferred to a previously evacuated, baked and sealed empty ampoule complete with PTFE tap. After the transfer, this second ampoule was resealed via the tap and glass-blown on to the manifold (Fig. 1). In order to avoid any subsequent water vapour contamination of the iodine, the manifold was then baked out up to the ampoule tap. This was then opened for a few





minutes to allow degassing of the iodine via an auxiliary liquid-nitrogen trap and oil diffusion pump (not shown in Fig.1) in order to remove nitrogen and any volatile impurities. The manifold was then scaled off from the auxiliary pump route via a constriction, and rebaked. The procedure described above was only carried out once, in order to provide a scaled ampoule of source material in position on the manifold prior to the first cell-filling operation.

In preparation for every filling operation, the manifold and cells are baked-out within the stainless-steel oven at a temperature of about 360 °C for 2 days. The oven is capable of controlled operation up to 500 °C. The section of pump line external to the oven is baked to about 300 °C using heater tapes, as is the short length of pyrex tube leading to the iodine ampoule. The temperature is monitored by thermocouples at various locations on the pump line, manifold and cells. The system pressure is monitored with an ionization gauge situated above the main oil diffusion pump and liquid-nitrogen trap, and after bake-out a pressure of about 3×10<sup>-6</sup> Pa is indicated. The diffusion-pump oil is of a silicone type, and a thermoelectrically-cooled baffle is situated between the pump and trap. Backstreaming of hydrocarbon vapour from the mechanical roughing-pump oil is limited by the use of an activatedalumina foreline trap.

Subsequent to this bake-out preparation, and immediately prior to opening the iodine ampoule to the cell manifold, the manifold is glass-sealed from the pump at a constriction in the main pump-line bore. The pressure rises to a few  $\times 10^{-5}$  Pa in this instance due to the local outgassing as the constriction is heated. It is necessary to ensure that the bulk of outgassed material is pumped away before the constriction fully seals. Iodine is then admitted to

the system, via the PTUE tap on the first fill, and via break-seal ampoules (see below) on subsequent tills The system manifold is kept at about 50 °C and the ampoule gently heated to assist rodine transfer. In turn, part of each cell body is cooled with div ice until a small amount of iodine is observed there That cell is then sealed at its side arm construction and removed from the manifold by glass-blowing After removal of the last cell, the empty break scal ampoule is similarly cooled with divice to condense out the remaining iodine in the manifold, scaled off and removed. This ampoule is then used as the iodine source in the subsequent batch fill. The use of break-seals rather than PTFF taps is preferred because of the higher-temperature bake-out then possible, and the greatly reduced likelihood of a leak across the seal.

#### 3. Verification of lodine Cells

Subsequent to each iodine fill, the absorption cells are tested for the presence of impurity gases existing within the cell. These tests use two different techniques, one of which assesses the frequency shift of the iodine hyperfine spectrum due to the foreign gas concentration. The other technique measures the related foreign gas pressure-broadening contribution to the linewidth of an iodine transition.

#### 3.1. Determination of Frequency Shift

To determine the frequency shift, cells are inserted into a 633 nm laser cavity and the laser is stabilized to a saturated-absorption feature in the iodine. The laser output frequency is tested, under standard operating conditions of iodine pressure and laser NRC Iodine Cells (G.R. Hames)

The NRC iodine cells are of fused quartz construction. Those containing  $^{127}\mathrm{I}_2$  were filled by the following method:

- 1. The cells were evacuated by a liquid nitrogen (LN2) trapped oil diffusion pump and heated strongly by torch to outgas.
- An excess of iodine was distilled from a reservoir where it was covered by

   a 2 cm layer of phosphorus pentoxide. The reservoir was at 20°C and
   the cell was at 0°C.
- 3. The excess iodine was pumped away.
- 4. The side arm of the cell was immersed in LN2 and the cell sealed off.

The cells containing  $^{129}I_2$  were filled by a similar method except that no phosphorus pentoxide was used, and the excess iodine pumped away in step 3 was very small, so the potential for contamination in these cells is much higher.

How to refine and fill iodine 127 into the cell at NRLM

T. Sakurai, S. Iwasaki, T. Kurosawa and K. Tanaka

#### INTRODUCTION

The refinement of iodine 127 was started from commercially available "solid" iodide reagent with a purity of better than 99.8 %. The purity of the iodine reagent was guaranteed through the inspection based on the Japanese Industrial Standards (JIS) concerning reagents. According to JIS, impurities in it were stated as non-volatiles of less than 0.01 %, sulfide of less than 0.01 %, harogen of less than 0.003 % ( chlorine equivalent ) and a trace. We have considered that the content of impurities was so that, presumably, we were not necessary to concern with small separation from the commercially available iodine their seriously. Instead, as it was well-known, serious problem was an unexpected mixing of water vapor with iodine when the cell was filled with it. Therefore when we transferred iodine from a commercially available small iodine-bottle to the iodine cell using a vacuum refinement method, we used "molecular ceaves ( model 4A)" as an adsorption reagent for water vapor. The molecular ceaves was a brand-name which were named to the adsorption reagent sold by the Union Carbide Co. Ltd., U.S.A. In the process of the vacuum refinement, we expected that noticeable amount of impurities must be extracted from iodine. We have not. confirmed the impurity content qualitatively by such an appropriate method as the laser induced fluorescence method, however, we have checked quality of the iodine cell through the SN ratio of the third derivative signal.

#### REFINEMENT

We used a multi-stages refinement using a vacuum vacuum system made of pyrexglass as indicated in Fig. 1. With two liquid-nitrogen-trap, CT and UT, the diffusion pump ( we call usually it Hickman pump) normally had a pumpingcapacity of obtaining pressure of better than 10-5 Pa at the end of the vacuum tubing, Ι, after careful baking for the vacuum system. Outline of the filling procedure will be described below.

1



Fig. 1. Vacuum system made of pyrex-glass. a,b: valves, I: ionization gauge, G: Geisler discharge tube, UT: U-type liquid-nitrogen-trap, CT: coaxial-type liquid-nitrogentrap, DT: diffusion pump, UL: U-type desiccator, RP: connected to rotary pump.

1.5

Note The spelling of "molecular ceaves" should be chucked. A) The first refinement

Figure 2 shows a pyrexglass assembly for the first refinement which was connected to a port P1 in Fig.1 using a city-gas torch with oxygen. In Fig.2, before the connection, commercially available iodine iodine ( the manufacturer of used had declared that its purity was better than 99.99 % ) of about 40 grams was filled into a vessel A. Molecular ceaves 4A of about 5 grams was into a vessel, C. The filled procedure for the first refinement is as follows:



Fig. 2. The first refinement assembly made of pyrex-glass. A: vessel filled with the original iodine 127, B: vessel for pre-fractionation, C: vessel for molecular ceaves, D: sample cell depositing the refined iodine, s: breakable seal.

1) Cooling A with liquid nitrogen and baking C with a electric heater, E, at 450 °C, a careful pumping was continued for at least three days. Then we obtained a pressure of order of 10-4 Pa in the vicinity of A.

2) Taking E off and cooling a vacant vessel B with liquid nitrogen, pumping was still continued till a small amount of iodine ( about 5 grams) was trapped in B. Then sealing necks, b and t, were melted with a torch, B and whole the glassassembly shown in Fig.2 were taken off from the vacuum system. We considered that iodine trapped in B must contain impurities with a higher concentration than that in A.

3) Keeping the glass-assembly at room-temperature and cooling a sample cell D with ice. Then iodine in A started to fly to D through molecular ceaves. After a half of iodine in A was transferred to D, D was taken off from the glass-assembly. Iodine in the sample cell D was the refined one; we called it "the first sample cell".

#### B) The second refinement

Figure 3 shows a glassassembly for the second refinement. The first sample cell was connected to it as indicated in Fig.3. The glass-assembly was connected to the vacuum system again and was pumped. In Fig.3, H is a "bullet" which is a cylindrical permanent magnet wrapped by pyrex-glass. The bullet can translate using a conventional U-type magnet and break a "breakable seal", s. G1 to G6 are small cells into which the re-refined iodine is filled. The procedure for the second refinement is as follows:



Fig. 3. The second refinement assembly made of pyrex-glass. C: vessel for molecular ceaves, D: sample cell filled with the refined iodine, G: small sample cells depositing the secondary-refined iodine, H: bullet to break the seal s. 1) Using a electric heater, G1 to G6 and a vessel C, in which molecular ceaves was filled, was pumped carefully.

2) After reaching a pressure of 10-4 Pa, a sealing neck, r, was melted and whole the glass-assembly shown in Fig. 3 was taken off from the vacuum system.

3) Keeping the assembly at room temperature and cooling the bottom of G1 to G6 with ice, iodine in D flied to G1 to G6 if s was broken by H.

4)After crystal of iodine in G1 to G6 was grown to a size of 0.5 to 1 mm3, G1 to G6 were taken off from the glass-assembly using a torch; we called these small cells "the second sample cell".

C) Iodide absorption cell

Figure 4 shows the final stage to fill the iodine cell with iodine. G is the second sample cell. Using almost the same fashion with molecular ceaves C, iodine was transferred to the cell and sealed off. Figure 5 shows a typical third derivative signal taken with the iodine cell which was filled by means of the present method.



Fig. 4. the final stage for filling the refined iodine to the iodine cell. G: small sample cell filled with the secondary-refined iodine, E: electric heater.



Fig. 5. Typical third derivative signal of the hyperfine components d to .i . The refined iodine with the isotope ratio natural was filled in the iodine absorption cell. The temperature of the cell was 11 °C and the intracavity power 16 mW.

#### SUMMARY

We have not evaluated the present method qualitatively, however, the SN ratio of the third derivative signals obtained from our iodine cells is similar to the other activities reported by BIPM and many standard laboratories. It is noted that no change have been recognized in the SN ratio of the third derivative signals obtained from our iodine cells since more than ten years ago. We are expecting if our results will be confirmed through the present intercomparison organized by BIPM.



Pumping and heating oven 1 and oven 2 up to 400 °C for about 2 days. Cold trap cooled down with liquid nitrogen. Valve 1 and 2 open, 3 closed. Iodine reservoir cooled to about -60 °C with cooled alcohol. Valve 3 opened and system pumped to  $\langle 2 \cdot 10^{-6}$  mbar for about 2 hours. Ovens switched off and after cooling down to room temperature valve 3 is closed

and the iodine cooling container is removed. Valve 2 closed - valve 3 opened. Cooling of the iodine cell finger with ice water, cooled alcohol or liquid nitrogen. Waiting until sufficient iodine is sublimated into the cell finger. Closing of valve 3. Then opening of valve 2 and melting the cell immediately.

# IODINE CELL PREPARATION BIPM

## J.-M. Chartier and F. Perez

We buy our cells from HELLMA (Germany): they are made from fused quartz with an adaptation for pyrex .

The cells are cleaned using a chromic sulphuric acid mixture in an ultrasonic container, washed with distilled water, cleaned with a tri-sodium phosphate basic mixture in an ultrasonic container, washed with distilled water and then with pure alcohol. The cells are then dried in an oven at 120 °C before being blown on to the vacuum system.

Five or six cells are fixed to the vacuum system (see Figure), below. They are pumped using the vacuum system (VS2) and the nitrogen trap (NT2) : VS2 and NT2 are always kept clean, without iodine ; they are used only to outgas the cells at 350 °C using the electric oven during (EO) several days at a pressure of about around 1,33 x  $10^{-5}$  Pa (1 x  $10^{-7}$  Torr). During this operation valve V4 is closed and valve V5 is opened.



We use iodine from MERCK (Germany) having a purity of better than 99,8 %. Before fixing the iodine reserve (R1) on the vacuum system, the iodine is left in contact with phosphoric anhydride ( $P_2O_5$ ) to be dried.

The iodine is then distilled several times from R1 to R2, from R2 to R3 and from R3 to R2 to remove water vapour using the cold point method. Each cell is then filled with iodine using an alcohol and ice water mixture to cool the "cold finger" for several minutes and the cell is closed at a constriction prepared previously.

# Appendix III

Laboratory	Cell	Length / cm	Diameter / cm	Isotope
CSIRO	1	10	1,3	127
IMGC	2			•
	30			w.
INM	6	10	1,0	
	9			
	12	•		*
	D1			
	LAC	5	1,5	
KRISS	4	12	1,2	
	5	•	1,2	
	115	9	1,0	
NIM	п	12	1,0	
	ш			
NIST	1	10	1,2	-
NPL	5C	10	1,25	•
	MOM3e		M	
	MOM2b			
	5A			246.
NRC	7-12	12	0,8	( <b>#</b> )
	7-13		-	
	9-1	-		129
	9-2	•		
NRLM	1	10	2,0	127
	2			
	3		1,6	
РТВ	17/87	10	1,2	
	16/89			*
	7/90		-	κ.

Participating laboratories, identification of iodine cells, dimensions and isotopes.

Laboratory	Cell	Length / cm	Diameter / cm	Isotope	
		25			
BIPM	1	10	1,2	-	
	35	44	#		
	64	<u>#</u>	**		
	67	12,5	*	<	
	71	10	ac.	ан. Г	
	88	•	<u>u</u>	1627	
	95	*			
	106	15		. <u>1</u>	
	107	9	¥	ii.	
	112	10		и;	
	JAEGER	÷	-	2	



Most of the investigated cells, waiting to be measured. The variation in the direction of the Brewster windows and the cell dimensions are clearly visible.

# Appendix IV

The recordings below show the hyperfine components d, e, f, and g, of some of the tested iodine cells. These recordings are useful to check the quality of the signal-tonoise ratio, to monitor and eliminate any eventual bias voltage. Such a recording was obtained each time a new cell was mounted on the test laser.



### Appendix V

The design of the least-squares method to calculate the hyperfine component position from an over-determined system of equations is directly inspired by Åslund [i]. A larger but similar method is used to determine the term values of a molecular system in the molecular spectroscopy group at University of Stockholm. It treats a system of equations in matrix form.

The frequency difference  $v_1$  is measured by measuring the beat frequency between the hyperfine components  $a_1$  and  $b_2$ , that is,  $v_1 = a_1 \cdot b_2$ . Another measurement gives  $v_2 = a_2 \cdot b_1$ . Writing these two equations in matrix form, we have.

$$\begin{pmatrix} 1 & 0 & 0 & -1 \\ 0 & 1 & -1 & 0 \end{pmatrix} \times \begin{pmatrix} a_1 \\ a_2 \\ b_1 \\ b_2 \end{pmatrix} = \begin{pmatrix} v_1 \\ v_2 \end{pmatrix}$$
(A.1)

Extending the equation system to N measurements obtained between M components (N > M) we get the following :

$$\begin{pmatrix} 1 & 0 & \dots & 0 & -1 \\ 0 & 1 & \dots & -1 & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \vdots & \vdots & \ddots & \ddots & \vdots \\ 0 & 1 & \dots & 0 & -1 \\ 1 & 0 & \dots & -1 & 0 \end{pmatrix} \mathbf{x} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ \vdots \\ a_{M-1} \\ a_M \end{pmatrix} = \begin{pmatrix} v_1 \\ v_2 \\ \vdots \\ \vdots \\ v_{N-1} \\ v_N \end{pmatrix}$$
(A.2)

We write this equation as :

$$CA = v \tag{A.3}$$

where C represents the coefficient matrix, A represents the component frequency position to be calculated and the v matrix contains the measured frequency differences. Thus, by standard matrix algebra,

$$A = (C^T C)^{-1} C^T v .$$
 (A.4)

[i] N. Åslund, A data processing system for spectra of diatomic molecules, Arkiv för fysik, 1965, 30, 377-396.

The error  $s_i$  in the determination of the position of the component  $A_i$  can be written as:

$$s_i = \sqrt{(C^T C)^{-1}}_{ii} \sigma, \qquad (A.5)$$

where  $\sigma$  represents the standard deviation. The only thing that remains to be done before using the expressions above is to choose one of the components as origin.

# Appendix VI

Frequency differences obtained for all the cells between the BIPM7 and BIPM11 lasers.

Laboratory	Cell	(f <sub>bipm7</sub> -f <sub>bipm11</sub> ) / kHz
CSIRO	1	- 3,0
IMGC	2	- 0.94
	30	- 2.29
INM	6	- 1.89
	9	- 4.21
	12	- 6.88
	DI	- 6.20
	LAC	+ 11 29
KRISS	4	
(KSRI)	5	
	115	
NIM	Ш	+ 173
	ш	- 0.98
NICT	1	- 0,30
ND	1	+ 1,04
NTL	bC MOM2-	- 2,91
	MOM3e	- 10,20
	MOMZD	- 4,97
NDC	5A	- 8,25
NKC	7-12	- 10,60
	7-13	- 11,13
	9-1	
	9-2	
NRLM	1	- 9,90
	2	- 0,73
	3	- 1,89
РТВ	17/87	- 0,04
	16/89	+ 1,82
	7/90	+ 2,54
BIPM	1	
	35	- 1,51
	64	- 2,78
	67	- 7,18
	71	- 15,77

Laboratory

Cell

 $(f_{BIPM7} - f_{BIPM11}) / kHz$ 

95 - 6,92 106 - 7,54 107 - 2,27 112 - 5,2 JAEGER

-3,77s = 5,22

n = 31